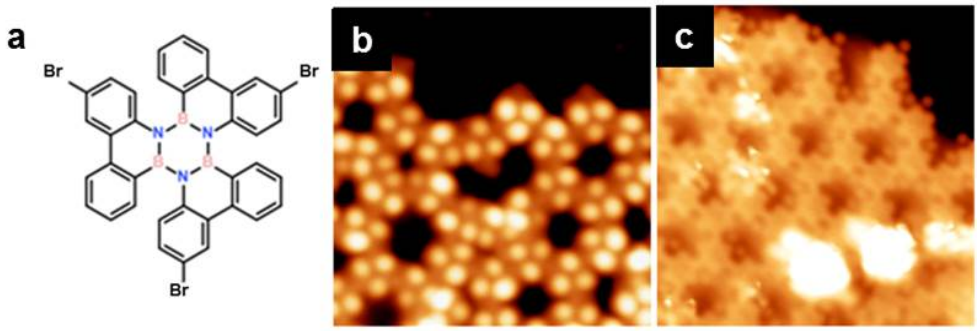


## *Charge-transfer Induced Isomerization Of DCNQI On Cu(100)*

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Cis-trans isomerization reactions have been recently proposed as models for the action of molecular-scale switches. Molecules like azobenzene derivatives have thus been deposited on solid surfaces and the isomerization reaction has been induced by external influences such as the tunneling current of an STM or light irradiation. Although the catalytic action of the surface on such reactions is amply acknowledged in previous works, understanding the exact mechanism of such reactions still requires further studies. Moreover, the effect of temperature on such reaction has not been studied at any extent. Here we show STM and DFT results on the thermally-controlled isomerization of the DCNQI molecules adsorbed on Cu(100). Depending on the substrate temperature two different molecular arrangements are observed, along with two different appearances of the molecules in STM images. Comparison with DFT calculations shows that whereas the low-temperature phase is consistent with a trans-geometry of the cyano groups with respect to the molecular axis, at higher temperatures such arrangement is formed exclusively with cis-isomers. The transition temperature, -30°C, is too low for the molecule in the neutral form to undergo such cis-trans isomerization, and thus a catalytic effect of the substrate must exist. Based on our experimental results and theoretical calculations we attribute such catalytic effect to charge-transfer from the metal to the molecule along with a strong bonding between the cyano groups and the copper atoms of the substrate. Charge-transfer lowers the cis-trans isomerization barrier in two synergistic ways. First it aromatizes the quinoid ring into a benzene ring, enabling a freer rotation of the cyano groups with respect to the molecular axis. Second, such easier rotation leads to an enhanced interaction of the cyano groups with the copper atoms of the substrate that brings the two isomeric forms closer to each other than in the gas phase conformation